

1087,477



# PATENT SPECIFICATION

NO DRAWINGS

1087,477

Date of Application and filing Complete Specification: Nov. 11, 1965.

No. 47927/65.

Application made in United States of America (No. 410,703) on Nov. 12, 1964.

Complete Specification Published: Oct. 18, 1967.

© Crown Copyright 1967.

PATENTS ACT, 1949

SPECIFICATION NO. 1,087,477

The following corrections were allowed under Section 76 on 20th February 1968

Page 2, line 10, after "constituents" insert closing bracket.

Page 2, line 11, for "cyclohexylphenyl)-" read "cyclohexylphenyl)-"

Page 2, line 13, after "phosphite" delete bracket

Page 5, line 45, for "tetliary" read "tertiary"

Page 5, line 47, for "a alkylidene" read "an alkylidene"

Attention is also directed to the following printers error:-

Page 5, line 17, for "xylene" read "xylylene"

THE PATENT OFFICE,  
20th May 1968

D 103433/17

25 phosphorous acid, notably trialkyl, triaryl or mixed aliphatic aromatic esters of  
phosphorous acid to prevent discolouration of high molecular weight linear thermo-  
plastic polycarbonates. 25

30 Despite this report, it has, nevertheless, been observed that tertiary esters of  
phosphorous acid such as triphenyl phosphites do not prevent discolouration of high  
molecular weight linear thermoplastic polycarbonate resins to as desirable an extent  
as might be desired. According to the present invention, however, it has been dis-  
covered that a combination of such tertiary esters of phosphorous acid with a highly  
hindered phenol provide especially effective protection against discolouration of the  
type which is prone to occur during heating of the resins. Quite surprisingly, the  
incorporation of both tertiary esters of phosphorous acid and highly hindered phenolic  
compounds in polycarbonate resins gives compositions which do not discolour nearly  
35 to the extent that polycarbonate resins discolour which contain either the phosphite or  
highly hindered phenol alone. Additionally, the compositions of this invention upon  
remolding evidence less change in melt viscosity than resins which do not contain the  
stabilizers. 35

40 In accordance with this invention, there are provided compositions of high mole-  
cular weight polycarbonates, especially linear thermoplastic polycarbonates of alkylidene  
bisphenols which contain both a tertiary ester of phosphorous acid (preferably tri-  
phenyl phosphite) and a highly hindered phenol usually in amounts of at least about  
0.05 per cent by weight of each additive based on the polycarbonate. Each of the  
respective additives may be present in the polycarbonate resin in amounts of up to  
45 5 per cent by weight of the polycarbonate. Typical concentrations are from 0.1 to 1 45

[Pric

SPECIFICATION AMENDED - SEE ATTACHED SLIP

BEST AVAILABLE COPY

**This Page Blank (uspto)**

1087,477



# PATENT SPECIFICATION

1087,477

NO DRAWINGS

Date of Application and filing Complete Specification: Nov. 11, 1965.

No. 47927/65.

Application made in United States of America (No. 410,703) on Nov. 12, 1964.

Complete Specification Published: Oct. 18, 1967.

© Crown Copyright 1967.

Index at acceptance:—C8 R (3C10, 3C12, 3C13, 3D14, 3D20, 3T2)

Int. Cl.—C 08 g 39/04, C 08 g 51/58

## COMPLETE SPECIFICATION

### Stabilising Polycarbonates

We, PITTSBURGH PLATE GLASS COMPANY, a Corporation organised under the laws of the Commonwealth of Pennsylvania, United States of America, of One Gateway Center, Pittsburgh, Pennsylvania, United States of America, (Assignee of ANDREW JOSEPH KAMAN), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns high molecular weight polycarbonate resins, notably high molecular weight linear thermoplastic polycarbonate resins of alkylidene diphenols such as di(monohydroxy-phenyl) substituted aliphatic hydrocarbons, of which 4,4'-dihydroxy-diphenylmethane (more commonly called Bisphenol A) is the best known. More specifically, the present invention concerns protecting such high molecular weight polycarbonate resins against discolouration and/or change in melt viscosity.

High molecular weight linear thermoplastic polycarbonates of Bisphenol A (such as are produced by the reaction of phosgene with Bisphenol A) tend to discolour and take on a strongly yellowish or brownish colour even though the polycarbonate originally is water white or near water white. This tendency towards discolouration seems particularly pronounced when polycarbonate resin is subjected to elevated temperatures. Since polycarbonates are widely used in injection molding where they are normally heated, this discolouration is likely to occur in a large field of use and hence is quite serious.

British Patent Specification No. 893,396 claims the use of tertiary esters of phosphorous acid, notably trialkyl, triaryl or mixed aliphatic aromatic esters of phosphorous acid to prevent discolouration of high molecular weight linear thermoplastic polycarbonates.

Despite this report, it has, nevertheless, been observed that tertiary esters of phosphorous acid such as triphenyl phosphites do not prevent discolouration of high molecular weight linear thermoplastic polycarbonate resins to as desirable an extent as might be desired. According to the present invention, however, it has been discovered that a combination of such tertiary esters of phosphorous acid with a highly hindered phenol provide especially effective protection against discolouration of the type which is prone to occur during heating of the resins. Quite surprisingly, the incorporation of both tertiary esters of phosphorous acid and highly hindered phenolic compounds in polycarbonate resins gives compositions which do not discolour nearly to the extent that polycarbonate resins discolour which contain either the phosphite or highly hindered phenol alone. Additionally, the compositions of this invention upon remolding evidence less change in melt viscosity than resins which do not contain the stabilizers.

In accordance with this invention, there are provided compositions of high molecular weight polycarbonates, especially linear thermoplastic polycarbonates of alkylidene bisphenols which contain both a tertiary ester of phosphorous acid (preferably triphenyl phosphite) and a highly hindered phenol usually in amounts of at least about 0.05 per cent by weight of each additive based on the polycarbonate. Each of the respective additives may be present in the polycarbonate resin in amounts of up to 5 per cent by weight of the polycarbonate. Typical concentrations are from 0.1 to 1

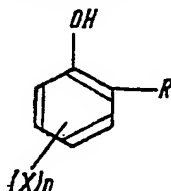
[Pric

BEST AVAILABLE COPY

per cent by weight of the polycarbonate resin for each additive. It is, however, rare that more than 2.0 or less than 0.1 weight per cent of the combination is employed. The polycarbonate resin may contain from 0.5 to 5 parts of the phosphite ester per part by weight of highly hindered phenol.

Esters of phosphorous acid which are useful may be generally characterized as tertiary esters of phosphorous acid, more particularly, trialkyl, triaryl, or mixed aryl alkyl esters, among which there may be mentioned tributyl phosphite, trioctyl phosphite, triphenyl phosphite, alkylated triphenyl phosphites (i.e. triphenyl phosphite esters in which one or more alkyl groups (notably lower alkyl groups containing from 1 to 10 carbon atoms) are linked to one or more of the phenyl constituents such as tri-(2-methylphenyl) phosphite, tri-(2-tertiary butylphenyl) phosphite, tri-(2-cyclohexylphenyl) phosphite, tri-(2,6-dimethylphenyl) phosphite, tri-(2-methyl-4-tertiary butylphenyl) phosphite, di(hydroxyethyl) cresyl phosphite, and diphenyl-hydroxyethyl phosphite.

By highly hindered phenols are meant phenolic compounds having a substituent on a phenyl ring carbon adjacent the carbon containing a phenolic hydroxyl group which deactivates the hydroxyl group. Illustrative hindered phenols are 2-alkyl phenolic compounds wherein the alkyl group contains from 4 to 10 carbons, and preferably is a branched alkyl chain. Thus, the highly hindered phenols can be depicted as having the following fundamental structural characteristic:



wherein R is a structurally large substituent, notably a branched alkyl substituent such as a tertiary butyl group or the like and n is 0 or an integer from 1 to 4. These phenolic compounds may contain other ring substituents. Thus, X may represent any of a large number of substituents linked to a ring carbon including hydroxyl, alkyl, phenyl and the like groups. One class of especially suitable hindered phenols are the diphenols, e.g., compounds having two phenyl groups each of which contains a phenolic hydroxyl group. The highly hindered phenol should be chemically inert and high boiling, to wit, have a boiling point above the melting point of the polycarbonate resin in which it is incorporated. Usually, this requires the highly hindered phenol to have a normal boiling point of at least about 200° to 250°C. and preferably higher, but rarely much above 400°C. Those highly hindered phenols which have normal melting points from 100° to 250°C. are especially easy to incorporate in the polycarbonate resin, although higher melting phenols can by special procedures also be utilized.

Various expedients may be relied upon to incorporate the appropriate amounts of tertiary ester of phosphorous acid and highly hindered phenol in the polycarbonate resin. Best results accrue when the additives are well if not substantially uniformly dispersed in the resin to thus provide what appears to be a homogenous composition. They may be added during the preparation of the polycarbonate resin, or preferably they are added after the resin has been prepared.

In one method of preparing polycarbonate resins, the polycarbonate resin is formed in a reaction medium containing a solvent for the polycarbonate resin. Hence, an organic solution of the polycarbonate resin is produced and is conveniently available. Both the phosphite ester and highly hindered phenol may be added to the polycarbonate solution, such as an organic solution of methylene chloride whereafter the methylene chloride solvent may be removed, for example, by a process such as described in Specification No. 924,756. The respective additives may also be either independently or as a mixture added to the polycarbonate resin subsequent to its production and incorporated therein, for example, by mixing when the resin is in powder or granular form.

The following Example illustrates polycarbonate resins which are protected pursuant to the present invention against colour degradation.

BEST AVAILABLE COPY

In the Example, the polycarbonate resin which was employed was a resin produced by controllably phosgenating Bisphenol A in the presence of aqueous sodium hydroxide solution and methylene chloride to produce an intermediate molecular weight bischloroformate polycarbonate of Bisphenol A which was then reacted with a quantity of piperazine which is slightly less than stoichiometrically equivalent to the chloroformate content of the intermediate weight chloroformate polycarbonate to produce a high molecular weight polycarbonate resin of the Bisphenol A, carbonic acid and the piperazine, the amount of piperazine moiety in the resin being approximately 0.1 that of the Bisphenol A on a mole basis. These polycarbonate resins have a K-value of 48.

#### EXAMPLE

To a resin prepared as immediately hereinbefore described, a stabilizer in the amount specified in Table 1 was incorporated and the resulting resin heated for 45 minutes at 340°C. in a stainless steel melt indexer (rigorous conditions of heating designed to evaluate on a laboratory scale the tendency of the polycarbonate to develop colouration). The stabilizers were incorporated by adding 50 milliliters of a petroleum ether solution of the additives to 100 grams of the resin in a powder form. The resulting mixture was mixed on rollers for 4 hours. The ether was then removed by heating in a 110°C. vacuum oven, first for 1 hour with a water aspirator, and then for 1 hour at 1 millimeter mercury pressure. The dried composition was then processed into pellets by extrusion, which pellets were dried at 110°C. under 1 millimeter mercury pressure for several hours. After being treated in the melt indexer, the polycarbonate composition was dissolved in methylene chloride to form a 3 per cent solution thereof, and the resulting solution's absorbency at 4000 angstroms was measured. The higher the absorption figure, the greater the discolouration. Table 1 lists these data:

TABLE I

Additive (Name)	Amount Weight %	Absorbency	
		Original	After Treatment
none	—	0.16	1.15; 0.92
Polygard*	0.10	0.14	1.51; 1.35
Polygard	0.20	0.13	0.71; 0.59
Polygard	0.50	0.11	0.90; 0.88
AO 431	0.30	0.14 (approximate)	1.47
Polygard AO 431	0.2 0.3	0.13	0.43; 0.37
Polygard AO 431	0.25 0.25	0.12	0.49
Polygard AO 431	0.35 0.45	0.14 (approximate)	0.44
Polygard AO 431	0.35 0.05	0.09	0.45
Polygard AO 431	0.15 0.05	0.10	0.49
Polygard Dalpac R*	0.2 0.3	0.12	0.60; 0.50
Polygard 2,5-di-t-butyl- hydroquinone	0.2 0.3	0.14	0.51; 0.51
2,5-di-t-butyl- hydroquinone	0.5	0.23	0.80

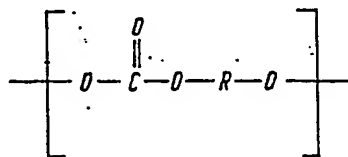
\*"Polygard" and "Dalpac" are Trade Marks.

Polygard is a commercial product of the Naugatuck Chemical Division of United States Rubber Company and is a tri(mixed mono- and dinonylphenyl) phosphite containing 4 weight per cent phosphorus.

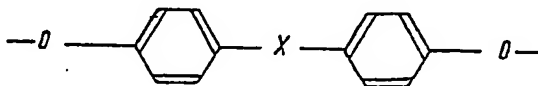
AO 431 is the chemical composition supplied by Naugatuck Chemical Division of United States Rubber Company as the antioxidant 431 and is principally 2,2'-bis (4-hydroxy-2,6-tertiary butylphenyl) propane.

Dalpac R is supplied by the Hercules Chemical Company and is principally the compound 2,6-di-t-butyl-4-methyl phenol.

High molecular weight polycarbonate resins which are protected against colour degradation pursuant to this invention are characterized by having as a major structural component the following recurring groups:



wherein R is a diphenol, particularly an alkylidene bis-phenol moiety:



X being an alkylidene group. Preparation of such polycarbonate resins, for example, by reaction of phosgene and an alkylidene bisphenol in the presence of a halogen halide acceptor such as sodium hydroxide and optionally an organic solvent such as methylene chloride is well described in the literature as are other methods by which such polycarbonate resins may be prepared.

Besides containing the hereinbefore described primary structural component, the polycarbonate resins may contain other moieties besides those of carbonic acid (i.e., carbonate group) and diphenols. Thus, besides being a polyester resin of carbonic acid and a bisphenol, the resin may contain moieties of other difunctional groups including diamines (which give rise to the presence besides carbonic acid linkages of carbamate linkages) and dicarboxylic acids including, for example, phthalic and isophthalic acids by way of illustration. Also, besides diphenols, other dihydroxy components may be incorporated into the resins, particularly glycols such as ethylene glycol, diethylene glycol, etc., as well as cycloaliphatic diols, e.g., xylene glycols.

Thus, the term "polycarbonate resin" as used herein refers to a polyester of carbonic acid and a diphenol, whether or not other moieties are present in lesser amounts.

#### WHAT WE CLAIM IS:—

1. A composition comprising a polycarbonate resin and, in combination, a tertiary ester of phosphorous acid and a highly hindered phenol.
2. A composition as claimed in claim 1, in which the polycarbonate is an alkylidene bisphenol polycarbonate resin.
3. A composition as claimed in claim 1 or 2, in which the ester of phosphorous acid is a phenyl ester.
4. A composition as claimed in claim 3, in which the phenyl ester is nuclearily alkylated.
5. A composition as claimed in any of claims 1 to 4, in which the phenol is 2,5-di-*t*-butyl hydroquinone.
6. A composition as claimed in any of claims 1 to 5, in which at least 0.05% by weight of each ingredient of the combination is included in the polycarbonate.
7. A composition as claimed in claim 6, in which up to 5% by weight of each ingredient of the combination is included in the polycarbonate.
8. A composition as claimed in claim 7, in which from 0.05 to 2% by weight of each ingredient of the combination is included in the polycarbonate.
9. A composition as claimed in any of claims 1 to 8, in which 0.1 to 1% by weight of each of phosphite and phenol is included in the polycarbonate.
10. A composition as claimed in any of claims 1 to 9, in which the combination is used in the ratio of 0.5 to 5 parts of phosphite per part by weight of phenol.
11. A composition as claimed in claim 1 substantially as hereinbefore described with reference to the example.
12. A method of improving the colour stability of a polycarbonate resin, which comprises dispersing in the resin a combination of a tertiary ester of phosphorous acid and a highly hindered phenol.
13. A method as claimed in claim 12, in which the polycarbonate is a alkylidene bisphenol polycarbonate resin.
14. A method as claimed in claim 12 or 13, in which the ester of phosphorous acid is phenyl ester.
15. A method as claimed in claim 14, in which the phenyl ester is nuclearily alkylated.

BEST AVAILABLE COPY

16. A method as claimed in any of claims 12 to 15, in which the phenol is 2,5-di-*t*-butyl hydroquinone.
17. A method as claimed in any of claims 12 to 15, in which at least 0.05% by weight of each ingredient of the combination is included in the polycarbonate.
- 5 18. A method as claimed in claim 17, in which up to 5% by weight of each ingredient of the combination is included in the polycarbonate.
19. A method as claimed in claim 18, in which from 0.05 to 2% by weight of each ingredient of the combination is included in the polycarbonate.
- 10 20. A method as claimed in any of claims 12 to 19, in which 0.1 to 1% by weight of each of the phosphite and phenol is included in the polycarbonate.
21. A method as claimed in any of claims 12 to 20, in which the combination is used in the ratio of 0.5 to 5 parts of phosphite per part by weight of phenol.
22. A method as claimed in claim 13 substantially as hereinbefore described with reference to the example.

W. P. THOMPSON & CO.,  
12, Church St., Liverpool, 1.  
Chartered Patent Agents.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.  
—1967. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2.  
from which copies may be obtained.

BEST AVAILABLE COPY